

Early Transition Metal Di- and Trichalcogenides: Structure and Bonding

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Layered transition metal dichalcogenides have long been the basis for numerous industrial processes, such as cathodes for non-aqueous lithium batteries [1,2] hydrocarbon processing catalysts and as lubricant additives [3,4]. Additionally, the electronic properties of metal dichalcogenides have been studied with regard to metal-insulator transitions [5], and charged density waves [6].

The early transition metal dichalcogenides adopt anisotropic structures [6] featuring two dimensional slabs which are comprised of two layers of chalcogen atoms sandwiching a metal layer. Depending on how these layers stack, the cation can have either trigonal prismatic or octahedral coordination. In d^0 complexes the metal prefer octahedral geometries while d^n ($n > 0$) metal complexes adopt trigonal prismatic geometries. Structural systematics has been explained in terms of local phenomena, e.g., electronegativity and ionic or covalent radii [10,11], as well as band structure calculation [7].

The synthesis and characterization of niobium triselenide in 1975 [8,9] opened a new and very promising area of research based on new two-dimensional substances. Early transition metal trichalcogenides are built up from $[MX_3]$ trigonal prismatic chains. These chains result from stacking of the distorted $[MX_6]$ prisms, allowing for the formation of chalcogen-chalcogen bonds. These bonds can have different bond lengths, making it possible to classify this class of compounds by the number of different chains per unit cell. The structural prototypes are $ZrSe_3$ (one kind of chain), $TaSe_3$ (two kinds of chains), and $NbSe_3$ (three kinds of chains). The chalcogen-chalcogen bond acts as an electron reservoir which has important effects on the electron density along the metallic chain [12].

Structural and XPS studies show that $(X_2)^{2-}$ and X^{2-} are present in all of these trichalcogenides which then can be formulated as $M^{4+}(X_2)^{2-}(X)^{2-}$ [13].

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